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Study of new absorption refrigeration cycle operating with partially miscible fluids pairs

Larkeche Ouassila[a*], Meniai Abedeslam-Hassan[a], Zermane Ahmed[a], Khatib Yacine[b] Cachot Thierry[c]

[a]*Laboratoire de l'Ingénierie des Procèdes de l'Environnement, Département de Chimie Industrielle, Université Mentouri, Constantine 25000, Algérie*

[b] Faculty of Engineering, King Abdelaziz University, Jeddah, Saudi Arabia.

[b]*Laboratoire des Sciences du Génie Chimique, Rue Grandville, BP451,54001,Nancy Cedex,France*

Abstract

In the present work a new configuration of absorption refrigeration machine based on phase separation has been studied. The main objective is to investigate the performance of this machine, using a number of binary systems (refrigerant-absorbent) showing a partial miscibility and having a low critical solution temperature. A computer code has been developed for the calculation of the coefficient of performance (*COP*) of the machine as well as to study the influence of the operating conditions on this parameter, testing a binary mixture made of methyl diethyl amine (*MDEA*) as refrigerant and water as absorbent. The obtained results confirm the feasibility of this new cycle which can be regarded as a good alternative to classical cycle with no phase separation. The use of the computer code can be extended to test different working fluids for this machine, for an optimisation of the *COP*.

Key words: absorption machine; *COP*; refrigerant; absorbent; refrigeration

1. Introduction

Depletion potential towards the ozone layer, emission of greenhouse gases, energy waste, are the major environmental problems, caused by the use of certain refrigerants. Therefore the use of renewable energy is a track widely explored along with the improvement of the energy efficiency of existing processes by developing environmental safe systems. The present study deals with a novel absorption refrigeration machine based on phase separation. Although this type of machine has been proposed a long time ago [1, 2] and present interesting features, it has not been extensively considered according to the few studies reported in the literature [3, 4]. However its major drawback is the selection of adequate binary fluids pairs which exhibit a good miscibility gap and hence offer a good performance. Consequently a general thermodynamic model has been developed in order to search for suitable fluid pairs. This model is based on the group contribution approach for the property calculations as well as the use of thermodynamic models such as *UNIFAC* and *NRTL* for the calculation of the activity coefficient required for the determination of the phase equilibria involved in the different compartments of the machine.

* Corresponding author. ***Tel/Fax: +213 (31) 81 88 80***

E-mail address: larkech_wassila@yahoo.fr

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Nomenclature

A Absorber
B The second coefficient of Virial
C_P Specific heat [J/mol]
CFC Chlorofluorocarbon
HCFC hydro chlorofluorocarbon
COP Coefficient of performance
E Evaporator
eps Solution heat exchanger efficiency
EV Expansion Valve
f fugacity
G Generator
H Molar enthalpy [joul /mol]
$\bar{h}$ Partial molar enthalpy [joul /mol]
HE Heat Exchanger
j conversion factor
m molar flowrate [mol/s]
MDEA methyl diethyl amine
P Pression [Pa]
PU Pump
Q Heat flow [W]
R Perfect gas constant
T Temperature[K]
V Molar volume[m3/mol]
x Molar fraction of the liquid
y Molar fraction of the vapour

Greek letters

ε_c Carnot cycle efficiency
ε_{HE} heat exchanger efficiency
γ_i activity coefficient

Superscripts

e Excess
L Liquid
M Mixture
V Vapour

Subscripts

a absorber
c critique
e evaporator
g generator
i component i
ii pure substance i
l liquid
v vapour
1 any number refers to a state point as shown in fig. 1

2. Description of the cycle

The absorption refrigeration cycle described in figure 1, is basically similar to the conventional cycle but the main difference is in the fact that the refrigerant does not have to be condensed after generator, because the steps of vaporization and condensation of refrigerant is eliminated and replaced by a simple liquid phase separation at higher temperature and pressure. The energy requirements are greatly reduced since creating a liquid- liquid phase separation requires much less energy than the boil off the more volatile component.
In this configuration of absorption cycle, a phase separation occurs in the generator, yielding two liquids phases, one rich in refrigerant (phase I) and the other poor in refrigerant (phase II).
Phase I (point1) is expanded and routed directly to the evaporator, the vaporized refrigerant (point3) leaving the evaporator (producing cooling effect) is mixed in the absorber with phase II coming from generator(point 9). The completely mixed liquid is compressed and heated again in the generator. A heat exchanger is incorporated between the generator and the absorption unit and operates counter-currently with phase (II) stream exiting the generator (point 7) and the solution coming out of the absorption unit (point 5).

The different points of the cycle are represented in the temperature-composition diagram figure 2.

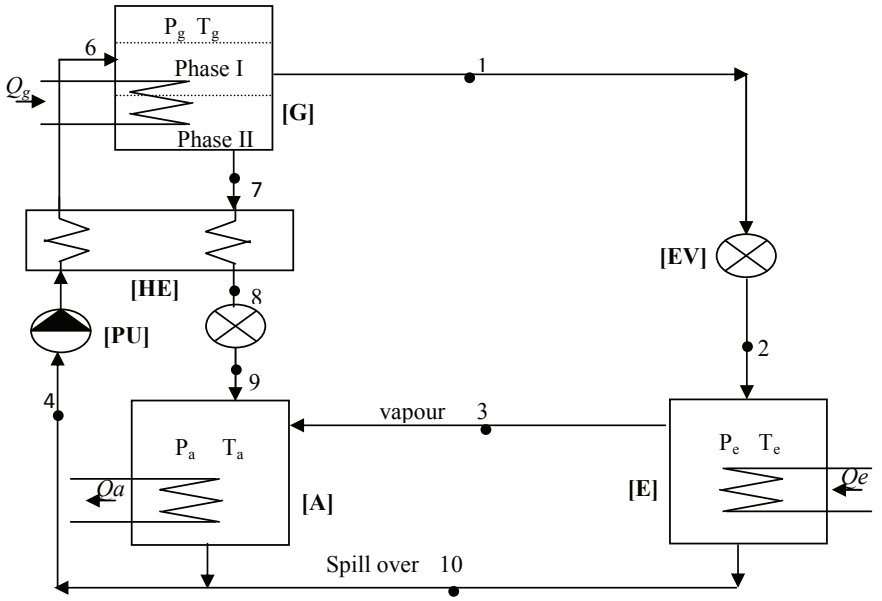

Fig1. Schematic diagram of Absorption- refrigeration cycle using phase separation.

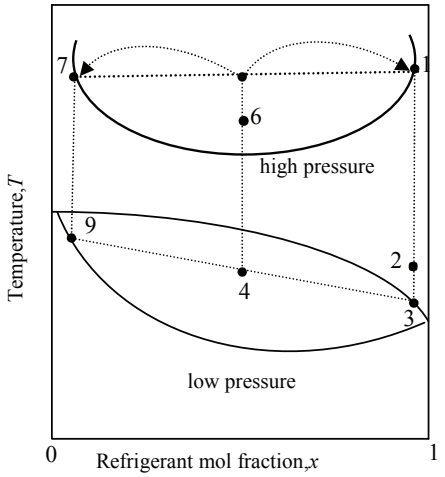

Fig 2. Representation of absorption-demixing refrigeration cycle in *T-x* diagram

3. Choice of working fluids

Suitable working fluids for this cycle are binary liquid mixtures (refrigerant-absorbent) which exhibit phase separation at reasonable temperatures, and have a lower critical solution temperature (*LCST*). The fluids pairs must have the proprieties required for conventional cycle summarized elsewhere [5]. Extended researches show that only few mixtures satisfy these characteristics. However some binary couples have been found, such as metyl diethyl amine- water mixture which selected to be tested here.

4. Thermodynamic model

The study of absorption cycle needs an accurate thermodynamic model in order to screen candidate working pairs according their qualitative criteria including thermo physical proprieties of the fluids and quantitative criteria such as *COP* of the cycle. The different steps of computer model for calculation of *COP,* in order to

investigate (*MDEA*+ water) mixtures, are presented. Due the availability of some experimental data, *NRTL* model has been adopted. To enable a thermodynamic study of the cycle, the proposed model has been based on number of hypotheses similar to ones reported in the literature in [4], [6] as follows:

- The cycle is operating in steady state;
- The temperatures in the generator, evaporator and absorber are supposed uniform in the considered volume;
- Pressure drop is neglected between the evaporator and the absorber, leading to the same pressure in both items;
- High and low pressures are equilibrium pressure at the generator and evaporator temperatures, respectively;
- Vapour-liquid equilibrium is assumed at the evaporator and absorber;
- The provided work to the pump is negligible;
- The expansions are supposed isenthalpic
- Heat and mass losses are negligible;
- The efficiency of the counter current heat exchanger is given by the following relationship:

$$\varepsilon_{HE} = \frac{T_6 - T_a}{T_g - T_a}$$

4.1 Phase equilibrium calculation

It is necessary to calculate liquid-liquid and vapour-liquid phase equilibrium of the considered system, in order to make easy the estimation of process conditions at all points in the cycle by assuming values for the evaporator, generator and absorber temperatures and pressures, and therefore the study of *COP* variations.

4.1.1 Liquid- liquid equilibrium

For the prediction of liquid phase separation, two methods were applied: the first is *Cox and Herington* model [7] which allows to define *LCST* of binary mixtures, while the second method is based on liquid phase equilibrium conditions by using of *NRTL* model.

Cox & Herington model [7]

Each branch of miscibility gap is described by the following equations:

$$T = T_C + \left[A' \log_{10}\left[(X_1'/X_2')\right] + B'\right]^3 \quad (1.a)$$

$$T = T_C + \left[A'' \log_{10}\left[(X_1''/X_2'')\right] + B''\right]^3 \quad (1.b)$$

Where X indicate the composition of each component in the two equilibrium phases, the critical temperature T_c and the constants: *A', A', B', B'*, must be regressed from experimental data [2]. The obtained results for the considered system are illustrated in figure 3 where it can be seen the concordance between the calculated results and experimental ones, the miscibility gap has a lower critical solution temperature of 323.15 K, this value has been confirmed by *Cox & Herington* model, therefore this model is recommended to predict consolute temperature mixtures.

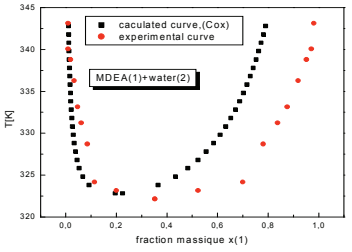

Fig.3. Miscibility gap of (*MDEA* +water) regressed by Cox equations

NRTL model

On the other hand, a simulation Fortran code using *NRTL* model has been performed, interaction parameters have been regressed from experimental data [2], for the considered binary mixture and the results are presented in figure 4, where a good agreement can be noted between the predicted results and experimental values.

Due to the large molecular weight difference of the two components *MDEA*- water, it must be specified that there is a difference whether representing the results in terms of mass or molar fractions, but this has no effect on the ultimate goal which is the phase compositions and the *LCST*.

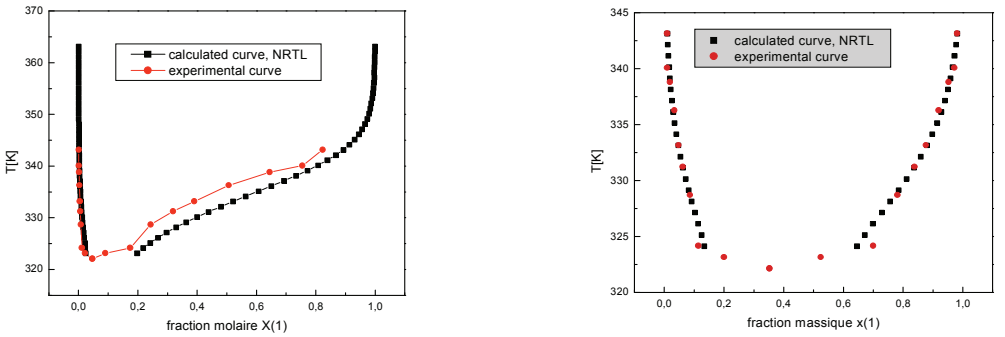

Fig.4. Miscibility gap of (*MDEA* +water) calculated by *NRTL* model

4.1.2 Liquid- vapor equilibrium

Liquid vapor predictions have been performed using the *NRTL* model for the calculation of the activity coefficient in the liquid phase and Viriel equation of state for the calculation of the fugacity coefficient in the vapour phase. The necessary critical proprieties are extracted from data bank *DIPPR*[8] and Antoine equation has been used to calculate vapor pressure [9].

Vapour- liquid equilibrium takes place in the evaporator and absorber. Consequently isothermal and isobaric equilibrium have been predicted and the results of *MDEA*-Water system are shown on Figure5a (*Tvs x,y*) and 5b (*P vs x,y*), and compared with experimental data available in [10]. A good concordance is noted confirming the reliability of the model.

Note that these diagrams can be used to solve the problem of operating conditions (pressure, temperature).

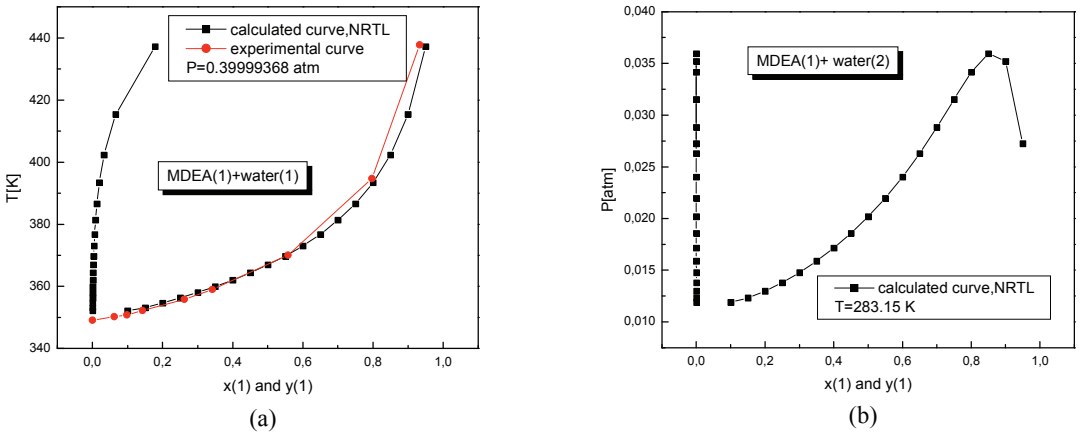

Fig.5. Vapour liquid equilibrium diagrams :(a)T*xy* ;(b) P*xy*

4.2 Enthalpy concentration diagrams

In order to evaluate the *COP,* enthalpies in liquid and vapor phases in terms of temperature, pressure and concentration, are required and are calculated according to the following expressions [11]:

$$h^V = \sum_{i=1}^{n} y_i \cdot \overline{h_i^V} = \sum_i y_i \cdot h_i^* + \left(B^M - T \cdot \frac{dB^M}{dT} \right) \cdot \frac{P}{j} \qquad (2)$$

$$h^L = \sum_{i=1}^{n} x_i \cdot \overline{h_i^L} = \sum_i x_i \cdot h_i^* + h^E + \sum_i x_i \cdot \left[-\frac{T}{j} \cdot \left(B_{ii} + \frac{R \cdot T}{P} - V_i^{0L} \right) \cdot \frac{dP_i^S}{dT} + \left(B_{ii} - T \cdot \frac{dB_{ii}}{dT} \right) \cdot P_i^S + \left(V_i^{0L} - T \cdot \frac{dV_i^{0L}}{dT} \right) \cdot \left(P - P_i^S \right) \right] \qquad (3)$$

The reference enthalpy h_i^* given at 0°C is calculated as follow:

$$h_i^* = h_0^* + \int_0^T Cp^0 \cdot dT \qquad (4)$$

Where $Cp^0(T)$ is specific heat calculated by using equation *(5)* [7], the constants *A,B,C,D,*E are extracted from *DIPPR* data bank.

$$Cp = A + B.\left(\frac{(C/T)}{\sinh(C/T)} \right)^2 + D.\left(\frac{(E/T)}{\cosh(E/T)} \right)^2 \qquad (5)$$

While the excess enthalpy is calculated as follows:

$$h^E = R \cdot T \cdot \sum_i x_i \cdot \ln \gamma_i - R \cdot T \cdot \left(\sum_i x_i \cdot \ln \gamma_i \right) - R \cdot T \cdot \left(\sum_i x_i \cdot \ln \gamma_i + T \cdot \sum_i x_i \cdot \frac{\partial \ln \gamma_i}{\partial T} \right) \qquad (6)$$

The activity coefficient γ_i of component *i* in the liquid mixture is calculated using the *NRTL* model.

4.3 *Heat and mass balances*

In order to develop the *COP* expression, heat and mass balances have to carry out over each essential part of the refrigeration unit *i.e.* the generator, the evaporator and absorber. The results are summarized in Table1.

Table 1. Heat and mass balances

Item	Global mass balance	Individual mass balance	Heat balance
Generator	$m_6 = m_7 + m_1$	$m_6 \cdot X_6 = m_7 \cdot X_7 + m_1 \cdot X_1$	$m_6 \cdot h_6 + Q_g = m_7 \cdot h_7 + m_1 \cdot h_1$
Evaporator	$m_2 = m_3 + m_{10}$	$m_2 \cdot X_2 = m_3 \cdot X_3 + m_{10} \cdot X_{10}$	$m_2 \cdot h_2 + Q_e = m_3 \cdot h_3 + m_{10} \cdot h_{10}$
Absorber	$m_9 + m_3 = m_4$	$m_9 \cdot X_9 + m_3 \cdot X_3 = m_4 \cdot X_4$	$m_9 \cdot h_9 + m_3 \cdot h_3 = m_4 \cdot h_4 + Q_a$
Notes	$m_7 = m_{II}$; $m_1 = m_I$; $h_1 = h_2$		

The *COP* is the main important parameter of an absorption refrigeration system and is defined as:

$$COP = \frac{Useful\ energy(cooling\ provieded\ in\ the\ evaporator)}{paid\ energy(heat\ provided\ in\ the\ generator)}$$

Which in our case, yields: $COP = \frac{Q_e}{Q_g}$ *(7)*

Consequently and referring to Figure 1, the *COP* can be expressed as follows:

$$COP = \frac{m_3 \cdot (h_3 - h_2) + m_{10} \cdot (h_{10} - h_2)}{m_7 \cdot (h_7 - h_6) + m_1 \cdot (h_1 - h_6)} \quad (8)$$

So for calculation of *COP* values, enthalpy has to be calculated at each point of the cycle (especially in those which appear in *COP* expression).

5. Cycle calculation

In the last section, all necessary equations to perform the calculation of *COP* were written and they are now used in the development of the computer program performing the calculation of the cycle and simulation of its coefficient of performance.The computer model is illustrated by the flow diagram shown in Figure 6 which describes the various stages executed to lead to the *COP* of the machine.

5.1 Operating conditions of the cycle

The enthalpy calculations require the determination of operating conditions such as temperature and pressure at each point of the cycle, as well as the mixture composition and the thermodynamic state.

Operating conditions depend on the machine application, so their choice is a crucial step. In the literature there are little information about considered absorption refrigeration system therefore a study of the optimizing operating conditions and screening of their influence on the cycle performance has been established.

The generator temperature depends on residual heat sources used and it should be higher than the *LCST* (in order to get phase separation). Its choice will depend on the results of phase separation where a large refrigerant concentration difference is desired for the phases entering the evaporator and entering the absorber.

Moreover as it has been explained in the last section, refrigerant in the strong phases will be evaporated in the evaporator and thereby the liquid concentration decreases at constant pressure until exit temperature is reached. In the absorber the vapor coming out of the evaporator is absorbed by weak liquid phase coming from the generator, and hence the concentration changed at constant pressure until equilibrium is reached. Consequently assuming evaporator temperature enables to deduce low pressure of the cycle, by using isothermal vapour -liquid equilibrium diagram and rich refrigerant concentration resulting from phase separation. So the pressure prevailing in the absorber is determined and enables to deduce absorber temperature, by using isobaric vapour-liquid equilibrium and poor refrigerant concentration resulting from phase separation too. The evaporator temperature was fixed arbitrarily for a cooling effect and its application. For the calculations in this work, three levels of temperatures were chosen (277.15, 280.15 and 283.15 *K*).

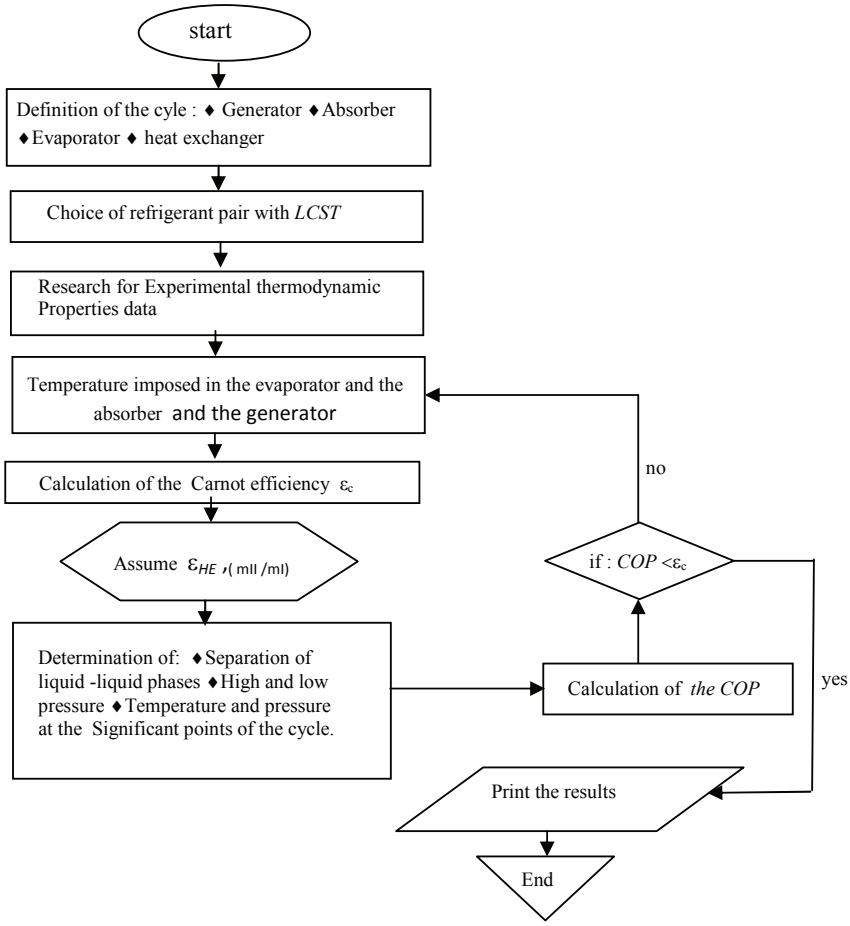

Fig. 6. Flow chart of simulation of the *COP* of the cycle

5.2 Parameter optimization

The Carnot efficiency is the maximum possible one for an absorption refrigeration system under given operating conditions. The Carnot efficiency for considered cycle is expressed by:

$$\varepsilon_c = \frac{T_e}{T_G} \cdot \frac{T_G - T_a}{T_a - T_e} \qquad (9)$$

Since the *COP* values cannot exceed the Carnot efficiency, it is proposed to study the *COP* evolution as function of the circulation ratio (m_{II}/m_I), and optimize the feasibility range of the cycle operating conditions by taking Carnot coefficient as a limit.

6. Simulation results and discussion

In order to simulate the influence of operating conditions on coefficient performance different numerical experiments were carried out, at different conditions (temperatures and pressures) using the elaborated model.

Figure 7 shows the influence of the generator temperature on *COP* cycle at different values of evaporator temperatures. It can be seen, that *COP* values increase when the generator temperature increases and reach the maximum at the highest evaporator temperatures.

This variation can be explained by the energies used in order to increase temperatures in generator and evaporator, to which the *COP* is directly linked eq.(7). In other terms we can say that when the temperature of the generator increases its thermal load rises and therefore the performance of system decreases.
On the other hand, Figure 8 shows that the *COP* has an optimum value at T_g=*343.15K*, for the three considered evaporator temperatures. This can be explained by the separation phases diagram illustrated in Figure.4.a where it can be seen that in the range of T_g=343.14*K* the concentration of the refrigerant remains constant in each phase of miscibility gap. Therefore it can be concluded that a large miscibility gap leads to high *COP* values.

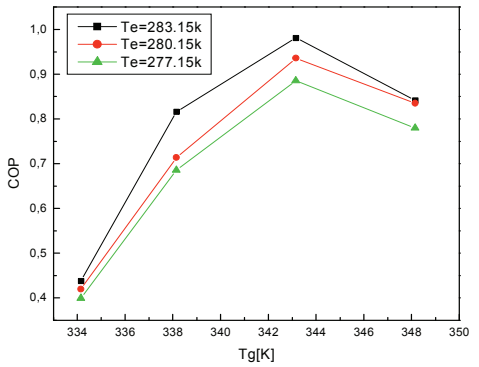

Fig. 7 Influence of generator temperature on cycle performance

Furthermore, the coefficient performance of the cycle is calculated as function of the flow rate circulating between (generator/ absorber) compartments denoted (m_{Π} /m_I)as shown in figure 8, where the *COP* decreases with the increase of circulation ratio. When circulation ratio increases the thermal loads of both generator and absorber increases, decreasing the *COP*. Thus a small circulation ratio leads to high *COP* values.

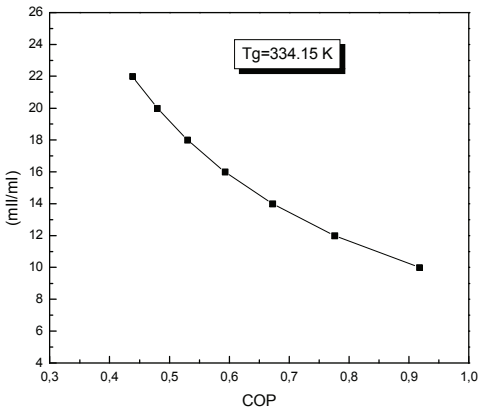

Fig. 8 Circulation ratio as function of *COP*

In order to validate the present computer model, a comparison is shown, through the results of the study of the effect of evaporator temperatures on *COP* at fixed generator temperature (T_g=334.15K) reported by Stephen and al. in [3].

The obtained results are close enough as shown in Figure 9. It can be deduced as expected that the increase of cooling effect necessity provides the increase of performance coefficient. The evaporator temperature affects the low pressure of the system. If the evaporator temperature raises the concentration of the weak solution and the circulation ratio decreases, the evaporator thermal load as well as the *COP* increases.

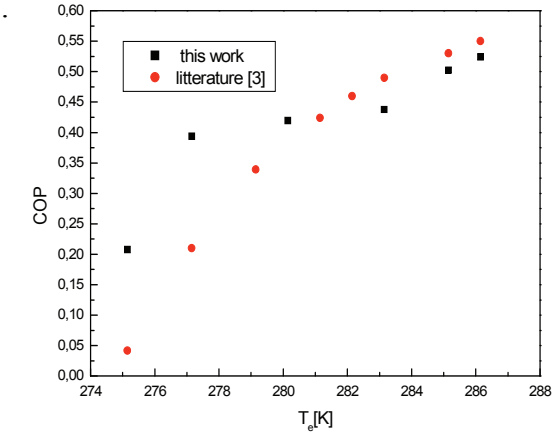

Fig.9: Influence of evaporator temperature on cycle performance

7. Conclusion

In this paper a thermodynamic model was presented to investigate the performance of absorption refrigeration cycle with phase separation, using *MDEA- water* binary mixture as working fluids. A relevant experimental data have been found in the literature so the *NRTL* model has been used for the prediction of phase separation and vapor liquid equilibrium. The results are close to the experimental values. The model evaluates the performance coefficient of this system at different operating conditions and the obtained results confirm the feasibility of this configuration of the absorption refrigeration cycle and the possibility of using *MDEA*- water as working fluids. A simulation code can be used for screening of suitable working fluids but results remain predictive, because this approach has to be validating by experimental work, where additional property should be considered such as: economy, chemical and physical stability, non toxicity, availability, and environmental safety factors, etc.

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